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ELECTRONIC STATES OF DIATOMIC MOLECULES;  
THE OXYGEN MOLECULE

by

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# ELECTRONIC STATES OF DIATOMIC MOLECULES: THE OXYGEN MOLECULE<sup>+</sup>

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## Abstract

A scheme is proposed for the computation of electronic energy levels of diatomic molecules with fair accuracy and minimum labor. The theoretical LCAO MO method including configuration interaction is employed. However, the number of configurations considered is kept small, the energies of the asymptotic dissociation products for the various states are taken from atomic data in the manner of Pariser, the calculation of the interaction energies is simplified by the neglect of overlap in all terms and the neglect of differential overlap in the electronic repulsion terms, and certain core parameters are fitted empirically. The first application is made to the oxygen molecule, using one empirical parameter. The vertical excitation energies from the ground state to the  $1\Delta_g$ ,  $1\Sigma_g^+$ ,  $3\Sigma_u^+$  and  $3\Sigma_u^-$  states are computed as functions of distance between 1.16A and 1.63A, and they agree with the observed values within 0.2 ev; excitation energies to the unobserved  $1\Sigma_u^-$ ,  $3\Delta_u$ ,  $1\Delta_u$  and  $1\Sigma_u^+$  states are also computed. The results are in substantial agreement with a previous more involved calculation by Moffitt. A justification of the proposed scheme is presented which makes use of the orthonormalized atomic orbitals of Löwdin.

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1.- The availability of a large amount of accurate experimental data on the electronic levels of diatomic molecules provides an ideal background for theoretical work, and yet few quantitative calculations have been made on diatomic molecules other than hydrogen since the early applications of variational techniques. The present work is not of comparable rigor but rather involves the development and application of a scheme to compute with minimum labor and fair accuracy electronic excitation energies in diatomic molecules involving several valence electrons, without necessarily obtaining a good approximation to the ground state.

The scheme is essentially the one proposed by Pariser and Parr<sup>1</sup> for the computation of the energy levels of complex unsaturated molecules. It falls within the framework of one-electron theories and uses the formalism of molecular orbital theory in the approximation in which molecular orbitals (MO) are expressed as linear combinations of atomic orbitals (LCAO). However, we consider the possibility that molecular states might not be properly described in simple configurational language, where a configuration is defined by assigning electrons to MO's -- we allow for configuration interaction. The choice of molecular orbital language is suggested by the availability of much outstanding qualitative work by Mulliken and others on the interpretation of the electronic spectra of diatomic molecules in terms of MO configurations.

The important features of the scheme<sup>1</sup> are the obtainment of the energies of the asymptotic dissociation products of molecular states from atomic data<sup>2,3</sup>, a considerable simplification of molecular algebra<sup>4</sup> effected by the neglect of overlap in the core terms and the neglect of differential overlap in the electronic repulsion terms, and the treatment

of certain molecular core parameters as empirical quantities.

For a first application of the scheme we have chosen the oxygen molecule. Here the quantitative treatment is simplified by the possibility of accounting qualitatively for the low excited states on the  $\pi$ -electron approximation. Moffitt<sup>5</sup> and Meckler<sup>6</sup> have also recently treated  $O_2$ . Meckler was interested in the magnetic properties of the ground state of the molecule over a wide range of distance and used Gaussian atomic functions; consequently he had to include a large amount of configuration interaction. Moffitt set out to test conventional LCAO MO theory with configuration interaction, and he arrived at a preliminary formulation and made a first application of his important "atoms in molecules" idea. In his formulation one constructs molecular wave functions of proper behaviour at infinite distance; this is not required in the present formulation.

2.- The qualitative interpretation of the low excited states of  $O_2$ <sup>7</sup> involves only two configurations:

$$\begin{aligned} A: & [(KK) (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2] (\pi_u 2p)^4 (\pi_g 2p)^2 \\ B: & [(KK) (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2] (\pi_u 2p)^3 (\pi_g 2p)^3 \end{aligned}$$

Indeed one can show by using the vector model and Pauli principle that the A configuration gives the states  $^3\Sigma_g^-$ ,  $^1\Sigma_g^+$  and  $^1\Delta_g$ , while the B configuration gives the states  $^3\Sigma_u^+$ ,  $^3\Sigma_u^-$ ,  $^3\Delta_u$ ,  $^1\Sigma_u^+$ ,  $^1\Sigma_u^-$  and  $^1\Delta_u$ . These include the observed low excited states of  $O_2$ .

It seems reasonable to try and develop a quantitative treatment of these states on the  $\pi$ -electron approximation<sup>5</sup>. There is then only one configuration to consider besides A and B:

$$C: [(KK) (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2] (\pi_u 2p)^2 (\pi_g 2p)^4$$

The choice of values for the one-center integrals  $(aa|aa)$  and  $(aa|s_s a_s)$  is a crucial point in the scheme. Moffitt<sup>2</sup> and Pariser<sup>3</sup> have independently pointed out that a major source of error in LCAO MO calculations of excitation energies using Slater AO's is the inaccuracy of the energies of dissociation products, and they have given ways of eliminating this error which involve taking data from atomic spectroscopy and using atomic wave functions only to compute the properly molecular part of the energy. We take this attitude and extend the method of Pariser<sup>3,1</sup>, determining the values of  $(aa|aa)$  and  $(aa|s_s a_s)$  from an analysis of the valence states of O, O<sup>+</sup> and O<sup>-</sup> which are relevant to the molecular states being considered. The identification of these valence states is schematically described in Table VI; Table VII gives their location in energy as derived from a Mulliken-type treatment<sup>9</sup>. Values of  $(aa|aa)$  and  $(aa|s_s a_s)$  are obtained by a least squares method from the following equations relating theoretical and experimental energy changes for dissociation processes:

$$\begin{aligned} 2 O(V_2) &= O^+(^1V_1) + O^-(V_1), (aa|aa) + (aa_s|aa_s) = 15.4 \\ 2 O(V_2) &= O^+(V_1) + O^-(V_1), (aa|aa) - (aa_s|aa_s) = 13.7 \\ 2 O(V_2) &= O^+(^3V_1) + O^-(V_1), (aa|aa) - 3(aa_s|aa_s) = 11.6 \end{aligned} \quad (6)$$

For the two center integrals  $(aa|bb)$  and  $(aa|b_s b_s)$  we take the values given by Kopineck<sup>10</sup> for Slater 2p $\pi$  AO's of effective charge 4.55. "Ball" values for these integrals<sup>4</sup> were discarded because they do not satisfy the identity,

$$(aa|bb) - (aa|b_s b_s) = 2(aa_s|bb_s), \quad (7)$$

which relates integrals over Slater orbitals, and this identity is used in obtaining the one-center integrals from valence-state data. We have also found that lowering the values of  $(aa|bb)$  and  $(aa|b_5b_5)$  as suggested by Pariser and Parr<sup>1</sup> lessens the agreement with experiment of the final excitation energies.

The value of the core parameter  $\alpha$  is not needed for the calculation of the excitation energies. We choose to consider  $\beta$  an empirical quantity, fitting it to the observed excitation energy  ${}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^+$  obtained from Morse curves for these two states. The resulting values of  $\beta$  are included in Table V.

5.- Table VIII gives the electronic excitation energies from the  ${}^3\Sigma_g^-$  ground state to the low excited states of  $O_2$  calculated using the energy formulas of Tables III and IV and the values for the integrals given in Table V. The experimental values for the excitation energies quoted in Table VIII are obtained by plotting Morse curves for the ground state and for each of the excited states using the experimental values for the equilibrium distance  $r_e$ , the dissociation energy  $D_e$  and the harmonic vibration frequency  $\omega_e$ <sup>7,11</sup>. For the states  ${}^1\Sigma_g^+$  and  ${}^1\Delta_g$  the resulting experimental excitation energies are reliable to a few thousandths of an ev, but for the states  ${}^3\Sigma_u^+$  and  ${}^3\Sigma_u^-$  the precision drops to a few hundredths and a few tenths of an ev, respectively.

Our theoretical results agree with the experimental values within 0.2 ev. For the state  ${}^3\Sigma_u^-$ , however, the agreement is somewhat uncertain since the experimental values are not known accurately; anyhow, it is clear that for this state the  $\pi$ -electron approximation breaks down at the larger distances considered, as Moffitt<sup>5</sup> has also noted.

A comparison of our calculated values with those of Moffitt<sup>5</sup> reveals very good general agreement. The approximation of zero differential overlap may be said to be thus vindicated.

The predicted excitation energies to the non-observed states  $^1\Sigma_u^-$ ,  $^3\Delta_u$ ,  $^1\Delta_u$  and  $^1\Sigma_u^+$  should be somewhat qualified. We regard with some confidence the predictions for the states  $^1\Sigma_u^-$  and  $^3\Delta_u$ , which should be stable and have a value for  $D_e$  of the order of 1 ev. The predictions for the more excited states  $^1\Delta_u$  and  $^1\Sigma_u^+$ , on the other hand, probably have only a qualitative value, giving the general location and the order in energy of these two states; whether they should be stable remains an open question.

#### APPENDIX

##### A justification of the scheme

The features of the scheme that need to be justified are the neglect of overlap in all energy terms and the neglect of differential overlap in the electronic repulsion terms, together with the use of Slater AO's to compute the integrals which are not assumed equal to zero.

Lowdin<sup>11</sup> has proved elegantly that his orthonormalized atomic orbitals ("Lowdin orbitals")<sup>12</sup>, which are defined to satisfy exactly the condition of zero overlap, satisfy approximately the condition of zero differential overlap. Here we shall consider in detail the case of diatomic molecules, deriving the relations between integrals over Lowdin orbitals and integrals over Slater orbitals. We shall see that the corrections are important only for the core integrals while for the electronic repulsion integrals the corrections may ordinarily be neglected.

Consider first a homonuclear diatomic molecule with equivalent Slater AO's  $\chi_a$  and  $\chi_b$  on the two atoms. Denoting by  $\lambda_a$  and  $\lambda_b$  the corresponding Löwdin orbitals we have

$$\begin{aligned}\lambda_a &= A\chi_a + B\chi_b, \\ \lambda_b &= B\chi_a + A\chi_b,\end{aligned}\tag{8}$$

where

$$A = + \sqrt{\frac{1 + \sqrt{1 - S^2}}{2 - S^2}} = 1 + \frac{1}{8} S^2 + \dots,$$

$$B = - \sqrt{\frac{1 - \sqrt{1 - S^2}}{2 - S^2}} = - \frac{1}{2} S + \dots,$$

in which  $S = \int \chi_a \chi_b dv$ . Then, denoting integrals over Löwdin orbitals by superscripts  $\lambda$ ,

$$S^\lambda = 0,\tag{9}$$

$$\alpha^\lambda = \frac{\alpha - S\beta}{1 - S^2} \sim \alpha,\tag{10}$$

$$\beta^\lambda = \frac{\beta - S\alpha}{1 - S^2} \sim \beta - S\alpha,\tag{11}$$

where  $\alpha = \int \chi_a H_{\text{core}} \chi_a dv$  and  $\beta = \int \chi_b H_{\text{core}} \chi_a dv$  are the Coulomb and resonance core integrals. The formula for  $\beta$  is indeed the one that Pariser and Parr<sup>1</sup> propose to apply in computing the core resonance integral to be used in the energy formulas whenever one does not want to consider this integral an empirical quantity. If we use the Mulliken<sup>8</sup> approximate formulas for the hybrid Coulomb-exchange and the exchange integral between  $\chi_a$  and  $\chi_b$  (tantamount to considering the first term in an infinite series expansion in powers of  $S^{13}$ ),



$$\begin{aligned}(aa|ab) &= \frac{1}{2}S [(aa|aa) + (aa|bb)], \\ (ab|ab) &= S (aa|ab),\end{aligned}\tag{12}$$

we obtain also

$$\begin{aligned}(aa|aa)^\lambda &= (aa|aa) + \left(\frac{S^2}{2-2S^2}\right) [(aa|aa) - (aa|bb)] \sim (aa|aa), \\ (aa|bb)^\lambda &= (aa|bb) - \left(\frac{S^2}{2-2S^2}\right) [(aa|aa) - (aa|bb)] \sim (aa|bb), \\ (aa|ab)^\lambda &= (ab|ab)^\lambda = 0.\end{aligned}\tag{13}$$

Suppression of the Mulliken approximation would cause terms in  $S^3$  to appear in these last formulas.

If each atom of the diatomic molecule carries two orthogonal Slater AO's say  $\chi_a$  and  $\chi_{a_s}$  on the first atom and  $\chi_b$  and  $\chi_{b_s}$  on the second, as in  $O_2$ , the argument can be generalized without difficulty. In particular, one finds that the integrals over Löwdin orbitals satisfy the identity, Eq. (7), which relates Slater orbitals.

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TABLE I. WAVE FUNCTIONS FOR SOME ELECTRONIC STATES OF O<sub>2</sub>.

Configuration	States	Wave Functions <sup>a</sup>	
A and C	3Σ <sub>g</sub> <sup>-</sup>	(π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>+</sup> π <sub>g</sub> <sup>-</sup> π <sub>g</sub> <sup>-</sup> π <sub>g</sub> <sup>-</sup> )	(π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>u</sub> <sup>-</sup> π <sub>u</sub> <sup>-</sup> π <sub>u</sub> <sup>-</sup> )
	1Σ <sub>g</sub> <sup>+</sup>	$2^{-\frac{1}{2}}[(\pi_u^+\pi_u^+\pi_u^+\pi_g^+\pi_g^-) - (\pi_u^+\pi_u^+\pi_u^-\pi_g^+\pi_g^-)]$	and $2^{-\frac{1}{2}}[(\pi_g^+\pi_g^+\pi_g^+\pi_u^-\pi_u^-\pi_u^+) - (\pi_g^+\pi_g^+\pi_g^-\pi_u^-\pi_u^+)]$
	1Δ <sub>g</sub>	(π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>-</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>-</sup> )	and (π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>-</sup> π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>-</sup> )
B	3Σ <sub>u</sub> <sup>+</sup>	$2^{-\frac{1}{2}}[(\pi_u^+\pi_u^+\pi_g^-\pi_g^+\pi_g^-) + (\pi_u^+\pi_u^-\pi_g^+\pi_g^+\pi_g^-)]$	
	3Σ <sub>u</sub> <sup>-</sup>	$2^{-\frac{1}{2}}[(\pi_u^+\pi_u^+\pi_g^-\pi_g^+\pi_g^-) - (\pi_u^+\pi_u^-\pi_g^+\pi_g^+\pi_g^-)]$	
	3Δ <sub>u</sub>	(π <sub>u</sub> <sup>+</sup> π <sub>u</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>+</sup> π <sub>g</sub> <sup>-</sup> )	
	1Σ <sub>u</sub> <sup>+</sup>	$2^{-1}[(\pi_u^+\pi_u^+\pi_g^-\pi_g^+\pi_g^-) + (\pi_u^+\pi_u^-\pi_g^+\pi_g^+\pi_g^-) - (\pi_u^+\pi_u^+\pi_g^-\pi_g^-\pi_g^-) - (\pi_u^+\pi_u^-\pi_g^-\pi_g^+\pi_g^-)]$	
	1Σ <sub>u</sub> <sup>-</sup>	$2^{-1}[(\pi_u^+\pi_u^+\pi_g^-\pi_g^+\pi_g^-) - (\pi_u^+\pi_u^-\pi_g^+\pi_g^+\pi_g^-) \cdot (\pi_u^+\pi_u^+\pi_g^-\pi_g^-\pi_g^-) + (\pi_u^+\pi_u^-\pi_g^-\pi_g^+\pi_g^-)]$	
	1Δ <sub>u</sub>	$2^{-\frac{1}{2}}[(\pi_u^+\pi_u^+\pi_g^+\pi_g^+\pi_g^-) - (\pi_u^+\pi_u^-\pi_g^+\pi_g^+\pi_g^-)]$	

Here (π<sub>u</sub><sup>+</sup>π<sub>u</sub><sup>+</sup>π<sub>u</sub><sup>-</sup>π<sub>g</sub><sup>+</sup>π<sub>g</sub><sup>-</sup>), for example, represents the normalized Slater determinant a typical term in the expansion of which is (π<sub>u</sub><sup>+</sup>α)<sup>1</sup>(π<sub>u</sub><sup>+</sup>β)<sup>2</sup>(π<sub>u</sub><sup>-</sup>α)<sup>3</sup>(π<sub>u</sub><sup>-</sup>β)<sup>4</sup>(π<sub>g</sub><sup>+</sup>α)<sup>5</sup>(π<sub>g</sub><sup>-</sup>α)<sup>6</sup>, where α and β are one-electron spin functions and superscripts denote electrons.

TABLE II. Energy formulas in terms of integrals  
over molecular orbitals.<sup>a,b</sup>

	$I(\pi_u)$	$I(\pi_g)$	$J(\pi_u^+, \pi_u^+)$	$J(\pi_g^+, \pi_g^+)$	$J(\pi_u^+, \pi_g^+)$
$3\Sigma_g^-(A)$	4	2	6	1	8
$3\Sigma_g^-(C)$	2	4	1	6	8
$H_{AC}$					
$1\Sigma_g^+(A)$	4	2	6	1	8
$1\Sigma_g^+(C)$	2	4	1	6	8
$H_{AC}$					
$1\Delta_g(A)$	4	2	6	1	8
$1\Delta_g(C)$	2	4	1	6	8
$H_{AC}$					
$3\Sigma_u^+(B)-$	3	3	3	3	9
$3\Sigma_u^-(B)$	3	3	3	3	9
$3\Delta_u(B)$	3	3	3	3	9
$1\Sigma_u^+(B)$	3	3	3	3	9
$1\Sigma_u^-(B)$	3	3	3	3	9
$1\Delta_u(B)$	3	3	3	3	9

<sup>a</sup> Except for the  $H_{AC}$ , the formulas given are for the energies of states of the indicated symmetries for the indicated configurations. The  $H_{AC}$  are interaction elements between the A and C configurations.

<sup>b</sup> Definitions of integrals are  $I(\phi) = \int \phi^* H_{core} \phi dv$ ,  $J(\phi_i, \phi_j) = \int \phi_i^*(1) \phi_j^*(2) (e^2/r_{12}) \phi_i(1) \phi_j(2) dv$ ,  $K(\phi_i, \phi_j) = \int \phi_i^*(1) \phi_j^*(2) (e^2/r_{12}) \phi_j(1) \phi_i(2) dv$  and  $(\phi_i \phi_i | \phi_i \phi_i) = \int \phi_i(1) \phi_i(2) (e^2/r_{12}) \phi_i(1) \phi_i(2) dv$ .

$K(\pi_U^+, \pi_U^-)$	$K(\pi_g^+, \pi_g^-)$	$K(\pi_U^+, \pi_g^-)$	$K(\pi_U^+, \pi_g^+)$	$(\pi_U^+ \pi_U^+   \pi_g^- \pi_g^-)$
-2	-1	-2	-2	0
-1	-2	-2	-2	0
		-1	1	
-2	1	-2	-2	0
1	-2	-2	-2	0
		1	1	
-2	0	-2	-2	0
0	-2	-2	-2	0
		0	1	
-1	-1	-3	-3	1
-1	-1	-3	-1	-1
-1	-1	-2	-3	0
-1	-1	-1	-1	1
-1	-1	-1	-3	-1
-1	-1	-2	-1	0

TABLE III. Energy formulas in terms of integrals over atomic orbitals -- A and C configurations.<sup>a,b</sup>

	$\frac{1}{4}(aa aa)$	$\frac{1}{4}(aa a_s a_s)$	$\frac{1}{4}(aa bb)$	$\frac{1}{4}(aa b_s b_s)$	Core Contribution
$3\Sigma_g^-(A)$	3	23	15	19	$6\alpha + 2\beta$
$3\Sigma_g^-(C)$	3	23	15	19	$6\alpha - 2\beta$
$H_{AC}$	-1	3	1	-3	0
$1\Sigma_g^+(A)$	7	19	19	15	$6\alpha + 2\beta$
$1\Sigma_g^+(C)$	7	19	19	15	$6\alpha - 2\beta$
$H_{AC}$	3	-1	-3	1	0
$1\Delta_g(A)$	5	21	17	17	$6\alpha + 2\beta$
$1\Delta_g(C)$	5	21	17	17	$6\alpha - 2\beta$
$H_{AC}$	1	1	-1	-1	0

<sup>a</sup> See Table II, note a.

<sup>b</sup> Definitions of integrals are  $(pq|rs) = \int \chi_p(1)\chi_q(1)(e^2/r_{12})\chi_r(2)\chi_s(2) dv$ ,  $\alpha = \int \chi_a H_{core} \chi_a dv$  and  $\beta = \int \chi_b H_{core} \chi_b dv$ , where  $\chi_p, \chi_q, \chi_r$  and  $\chi_s$  are Slater AO's from the set,  $\chi_a, \chi_{a_s}, \chi_b, \chi_{b_s}$ .

TABLE IV. Energy formulas in terms of integrals over atomic orbitals -- B configuration.<sup>a, b</sup>

	$\frac{1}{2}(aa aa)$	$\frac{1}{2}(aa a_s a_s)$	$\frac{1}{2}(aa bb)$	$\frac{1}{2}(aa b_s b_s)$	Core Contribution
$3\Sigma_u^+$	2	10	11	7	$6\alpha$
$3\Sigma_u^-$	1	13	8	8	$6\alpha$
$3\Delta_u$	2	10	9	9	$6\alpha$
$1\Sigma_u^+$	5	9	8	8	$6\alpha$
$1\Sigma_u^-$	2	10	7	11	$6\alpha$
$1\Delta_u$	3	11	8	8	$6\alpha$

<sup>a</sup> See Table II, note a.

<sup>b</sup> See Table III, note b.

TABLE V. Values of integrals (ev).<sup>a</sup>

	Internuclear Distance (A)					
	0	1.163	1.279	1.396 1.	1.512	1.628
(aa bb)	14.52	11.213	10.350	9.601	8.947	8.372
(aa b <sub>s</sub> b <sub>s</sub> )	12.62	11.019	10.216	9.507	8.880	8.324
		5.381	3.283	2.390	1.956	1.689

<sup>a</sup> See Table III, note b, for definitions of integrals.



TABLE VI. Valence states of  $O$ ,  $O^+$  and  $O^-$ .

State	Schematic $\pi^+$	Representation <sup>a</sup> $\pi^-$	Energy Formula <sup>b</sup>
$O^-, V_1$	$\circ \quad \circ$	$\circ \quad \circ$	$6J_{\pi\pi} - 2K_{\pi\pi} + 4\alpha(O^-)$
$O, V_2$	$\left\{ \begin{array}{c} \circ \quad \circ \\ \circ \quad \circ \end{array} \right.$	$\left\{ \begin{array}{c} \circ \quad \circ \\ \circ \quad \circ \end{array} \right.$	$3J_{\pi\pi} - K_{\pi\pi} + 3\alpha(O)$
$O^+, V_1$	$\left\{ \begin{array}{c} \circ \quad \circ \end{array} \right.$	$\left\{ \begin{array}{c} \circ \quad \circ \end{array} \right.$	$J_{\pi\pi} + 2\alpha(O^+)$
$O^+, {}^3V_1$	$\circ$	$\circ$	$J_{\pi\pi} - K_{\pi\pi} + 2\alpha(O^+)$
$O^+, {}^1V_1$	$\left( \begin{array}{c} \circ \quad \circ \end{array} \right)$	$\left( \begin{array}{c} \circ \quad \circ \end{array} \right)$	$J_{\pi\pi} + K_{\pi\pi} + 2\alpha(O^+)$

<sup>a</sup> An  $\circ$  in the  $\left\{ \begin{array}{c} \text{first} \\ \text{second} \end{array} \right\}$  column under  $\left\{ \begin{array}{c} \pi^+ \\ \pi^- \end{array} \right\}$  indicates occupancy of  $\left\{ \begin{array}{c} \pi^+ \\ \pi^- \end{array} \right\}$  by an electron of spin  $\left\{ \begin{array}{c} \alpha \\ \beta \end{array} \right\}$ . Brackets denote alternative, parentheses coupled situations.

<sup>b</sup>  $\alpha(O^-)$ ,  $\alpha(O)$  and  $\alpha(O^+)$  denote the core energies of a  $2p\pi$  electron in  $O^-$ ,  $O$  and  $O^+$  respectively.  $J_{\pi\pi}$  is the Coulomb integral,  $K_{\pi\pi}$  the exchange integral between two  $2p\pi$  electrons in  $O^-$ ,  $O$  or  $O^+$ , as the case may be.

TABLE VII. Energies of spectroscopic and valence states of O,  
O<sup>+</sup> and O<sup>-</sup> (ev.).

State	Energy	Details of Energy Calculation <sup>a, b</sup>
O <sup>+</sup> , $^1V_1 \approx O^+, 2p$	18.6	18.6 = 13.6+5.0, 5.0 from spectral data for O <sup>+</sup>
O <sup>+</sup> , $V_1 \approx O^+, 2D$	16.9	16.9 = 13.6+3.3, 3.3 from spectral data for O <sup>+</sup>
O <sup>+</sup> , $^3V_1$	14.7	14.7 = 13.6+1.1, 1.1 = $\frac{1}{2} \left[ \frac{2p-4s}{5} + \frac{2D-4s}{3} \right]$
O <sup>+</sup> , $^4S$	13.6	ionization potential of O
O, $V_2$	0.5	0.5 = $\frac{1}{4} \left[ \frac{1D-3p}{2} + \frac{1S-3p}{5} \right]$ , using spectral data for O
O, $^3P$	0.0	arbitrary energy zero
O <sup>-</sup> , $V_1 \approx O^-, 2p$	-2.2	negative electron affinity of O

<sup>a</sup> Spectral data for O and O<sup>+</sup> and the ionization potential and electron affinity for O are taken from Landolt-Bornstein Tables, Vol. I, 1950.

<sup>b</sup> In the two cases in which averages of spectroscopic states are taken, the averages are formed in such a way as to give energy values in agreement with those quoted by Moffitt (reference 5). Alternative averaging processes are possible which give slightly different results.

TABLE VIII. Electronic excitation energies in O<sub>2</sub> (ev).<sup>a</sup>

		Internuclear Distance (Å) <sup>b</sup>				
		1.163	1.279	1.396	1.512	1.628
$1\Delta_g$	calculated	0.98	0.86	0.72	0.59	0.48
	observed	1.01	0.94	0.84	0.73	0.62
$1\Sigma_g^+$	calculated	1.90	1.61	1.30	1.04	0.83
	observed	1.70	1.55	1.37	1.17	0.97
$1\Sigma_u^-$	calculated	10.39	5.85	3.80	2.75	2.09
	observed	—	—	—	—	—
$3\Delta_u$	calculated	10.59	5.98	3.90	2.81	2.14
	observed	—	—	—	—	—
$3\Sigma_u^+$	calculated	10.78	6.12	3.99	2.88	2.18
	observed	10.78	6.12	3.99	2.88	2.18
$3\Sigma_u^-$	calculated	11.14	7.37	6.01	5.57	5.46
	observed	11.26	7.94	5.91	4.65	3.83
$1\Delta_u$	calculated	13.16	9.84	7.81	6.55	5.73
	observed	—	—	—	—	—
$1\Sigma_u^+$	calculated	15.06	11.74	9.71	8.45	7.63
	observed	—	—	—	—	—

<sup>a</sup> Excitation energies are relative to the  $3\Sigma_g^-$  ground state.

<sup>b</sup> The equilibrium internuclear distance for the ground state is 1.208 Å.